

Fracturing of Subterranean Formations

This invention relates to the fracturing of subterranean formations and particularly, although not exclusively, relates to a method of fracturing a subterranean formation and materials therefor.

Hydrocarbons, such as oil and natural gas, are obtained from a subterranean geologic formation (i.e. a "reservoir") by drilling a wellbore that penetrates the hydrocarbon-bearing formation. This provides a partial flowpath for the oil to reach the surface. In order for oil to be "produced", that is travel from the formation to the wellbore (and ultimately to the surface), there must be a sufficiently unimpeded flowpath from the formation to the wellbore. This flowpath is through the formation rock which has pores of sufficient size, connectivity, and number to provide a conduit for the oil to move through the formation.

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However, in many cases, the formation rock has low permeability and so needs to be "stimulated" to improve its permeability. One known method of stimulation involves injecting chemicals through the wellbore and into the formation at pressures sufficient to actually fracture the formation, thereby creating a large flow channel through which hydrocarbons can more readily move from the formation and into the wellbore.

30 Hydraulic fracturing involves breaking or fracturing a portion of the strata surrounding the wellbore, by injecting a fluid into the wellbore directed at the face of the geologic formation at pressures sufficient to

initiate and extend a fracture in the formation. More particularly, a fluid is injected through a wellbore; the fluid exits the wellbore through holes (perforations in the well casing) and is directed against the face of the formation (sometimes wells are completely openhole where
5 no casing and therefore no perforations exist, so the fluid is injected through the wellbore and directly to the formation face) at a pressure and flow rate sufficient to overcome the minimum in situ stress to initiate and/or
10 extend a fracture or fractures into the formation. Often, a fracture zone, i.e. a zone having multiple fractures, or cracks in the formation is created, through which hydrocarbon can more easily flow to the wellbore.

15 Existing fracturing fluids are largely based on two technologies: cross-linked Guar polymer and visco-elastic surfactants. Both of these systems have significant temperature limitations with specialised guar systems capable of limited performance above 300°F.

20 Additionally, conventional Guar based fracture fluids use solid fluid loss reducing agents to prevent "leak off" (a process wherein fluid extends further into the fracture face than desired, thereby reducing the fluid pressure).
25 However, the introduction of solids to address the leak off problem can reduce the resultant permeability of the fracture zone and reduce production from the fracture once the well is brought back into production after the treatment.

30 There are numerous known types of other fluids used in fracturing, many of which have complex formulations which

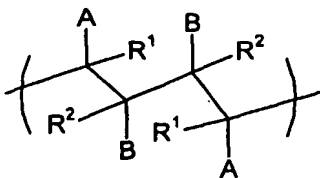
include various additives intended to address one problem or other.

It is an object of the present invention to address problems associated with fracturing of subterranean formations.

According to a first aspect of the present invention, there is provided a method of hydraulically fracturing a subterranean formation, comprising the step of:

contacting a subterranean formation with a treatment fluid formulation at a flow rate and pressure sufficient to produce or extend a fracture in the formation, wherein the treatment fluid formulation comprises a third polymeric material which comprises a second polymeric material cross-linked by a first polymeric material, wherein said first polymeric material comprises:

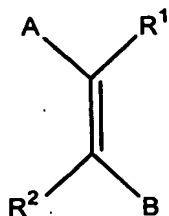
(i) a first polymeric material having a repeat unit of formula



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wherein A and B are the same or different, are selected from optionally-substituted aromatic and heteroaromatic groups and at least one comprises a relatively polar atom or group and R¹ and R² independently comprise relatively non-polar atoms or groups; or

(ii) a first polymeric material prepared or preparable by providing a compound of general formula



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wherein A, B, R¹ and R² are as described above, in an aqueous solvent and causing the groups C=C in said compound to react with one another to form said first
10 polymeric material.

Preferably, said first and second polymeric materials are reacted to form said third polymeric material prior to the treatment fluid formulation being injected via the
15 wellbore into the subterranean formation.

Preferably, prior to the treatment fluid formulation being injected, it has attained at least 50% of the maximum viscosity attainable for the formulation at the
20 temperature at which it is to be injected into the formation. Preferably, it has attained at least 65%, more preferably 90%, especially about 100% of its maximum viscosity. Thus, in the especially preferred embodiment, said first and second polymeric materials are
25 substantially completely reacted to form said third polymeric material prior to injection into the formation.

Said treatment fluid formulation preferably has a viscosity at 25°C in the range 50-500 cp, more preferably in the range 200-500cp, at a shear rate of 100s⁻¹.

- 5 The relatively high initial viscosity of the formulation may advantageously facilitate suspension of proppants (and other) materials therein.

Said treatment fluid formulation preferably has a
10 viscosity at 200°F in the range 20-100cp, more preferably of greater than 50 cp, measured at a shear rate of 100s⁻¹. Advantageously, the relatively high viscosity at high temperature may help to maintain fracture pressure, the effectiveness of the fracture process and also to minimise
15 fluid leak off.

Said treatment fluid formulation is preferably aqueous. It may include at least 90wt%, preferably at least 95wt% water. It preferably includes 90 to 99wt% water.

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Said treatment fluid formulation preferably includes one or more proppants. The formulation is compatible with any common proppant size required. The proppant may have a size in the range 20-40 mesh. Said proppant(s) may be
25 selected from sand, bauxite, man-made intermediate or high strength materials and glass beads. The proppant is arranged to restrict close down of a fracture on removal of the hydraulic pressure which caused the fracture.

- 30 The total weight of proppant(s) in said treatment fluid formulation is suitably in the range 5wt% to 30wt%. Preferably, the total weight of proppant(s) in said treatment fluid formulation is in the range 10 to 20 wt%.

Said treatment fluid formulation preferably includes breaker means for breaking the third polymeric material suitably to reduce its viscosity and facilitate clean up
5 of the fracture. Preferably, said treatment fluid formulation is arranged to break the formulation to enable it to be removed, by pressure within the formation, via the wellbore.

10 Said breaker means is preferably arranged to cleave chains of said third polymeric material, preferably chains thereof derived from said second polymeric material. Preferably, said breaker means comprises an oxidising agent arranged to cleave said chains. Preferably, said
15 breaker means is arranged to cleave 1,2-diol linkages. Said breaker means preferably comprises a periodate, especially sodium or potassium periodate. Suitably, at least 0.05wt%, preferably at least 0.1wt% of said breaker means is included. Suitably, 0.05 to 0.3wt% of said
20 breaker means is included.

Said breaker means may enable the viscosity to be reduced by a factor of at least 50%, preferably at least 70%, especially at least 90%.

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Said breaker means is preferably arranged to have a delayed action and suitably includes means for restricting contact between an active material (e.g. a material arranged to cleave chains of the third polymeric material)
30 and said third polymeric material. Said active material is preferably encapsulated.

Said breaker means preferably comprises crushable beads which incorporate said active material. Said breaker means is preferably arranged to be crushed to release said active material when the pressure of the treatment fluid formulation is reduced so that the fractures in the formation close down. When said treatment fluid formulation includes proppant(s) and breaker means it is preferred that the bead size of the breaker means is 0.75 to 3 times that of the proppant(s) and preferably is greater than the proppant size.

The breaker means is preferably adapted to resist breakage when passing through pumps or blending equipment that may be used in the fracturing method and when being subjected to the fracture pressure used in the method.

A crushable breaker means may be formed from glass, porous ceramics, plastics, gels or mixtures thereof.

As an alternative to (or in addition to) the active material being encapsulated by a crushable material, it may be encapsulated by a material which is arranged to release the active material via an alternative mechanism. For example, it may be arranged to rupture after prolonged fluid exposure or may slowly dissolve.

Said treatment fluid formulation may include 0.05 to 0.3wt% of crushable breaker.

Advantageously, the treatment fluid formulation may have very low solids content which should facilitate its use.

Preferably, the treatment fluid formulation includes less than 1 wt%, preferably less than 0.5 wt%, especially less than 0.25 wt% of fluid loss reducing agents.

- 5 In the method of the first aspect, the treatment fluid formulation may be contacted with a subterranean formation so that it attains a temperature of at least 200°C.

Said method preferably comprises selecting a said first
10 polymeric material; selecting a second polymeric material which includes a functional group which is able to react in the presence of said first polymeric material to form a third polymeric material; and causing the formation of said third polymeric material by a reaction involving said
15 first and second polymeric materials.

The ratio of the wt% of said first polymeric material to the wt% of said second polymeric material selected for preparation of said third polymeric material is suitably
20 less than 0.15, preferably less than 0.10, more preferably 0.8 or less. Said ratio may be at least 0.01, preferably at least 0.02, more preferably at least 0.025.

Preferably, the ratio of the wt% of said first polymeric
25 material to the wt% of said second polymeric material selected for preparation of said third polymeric material is in the range 0.025 to 0.067.

The sum of the wt% of the first and second polymeric
30 materials selected for preparation of said third polymeric material may be at least 1 wt%, preferably at least 2 wt%, based on the total weight of the treatment fluid

formulation. The sum may be less than 8 wt%, preferably less than 6 wt%, more preferably less than 4 wt%.

5 The sum of the wt% of the first and second polymeric materials selected for preparation of said third polymeric material is preferably in the range 1 to 6wt%, more preferably in the range 2 to 4wt%.

10 Suitably, the amounts of "first polymeric material" and "second polymeric material" described refer to the sum of the amounts of first polymeric materials (if more than one type is provided) and the sum of the amounts of second polymeric materials (if more than one type is provided).

15 Water for use in the treatment fluid formulation may be derived from any convenient source. It may be potable water, surface water, sea water, aquifer water, deionised production water and filtered water derived from any of the aforementioned sources. The water may be treated so
20 that it is suitable for use in the method. For example, it may be treated by addition of oxygen scavengers, biocides, corrosion inhibitors, scale inhibitors, anti-foaming agents and flow improvers. Sea water and/or water from other sources may be deoxygenated and/or
25 desulphonated.

In the preparation of said third polymeric material a catalyst is preferably provided for catalysing the reaction of the first and second polymeric materials.
30 Said catalyst is preferably a protic acid. Said acid preferably has an acid dissociation constant value of greater than 10^{-6} , more preferably greater than 10^{-4} and, especially, greater than 10^{-2} . A precursor formulation

which includes said first and second polymeric materials suitably includes less than 5 wt%, preferably less than 2wt%, more preferably less than 1 wt%, especially less than 0.5 wt% of catalyst. In a preferred embodiment, said treatment fluid formulation has a pH in the range 6 to 8 and is preferably neutral. Thus, the method may include a neutralisation step after addition of said catalyst.

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In the materials described above, A and/or B could be multi-cyclic aromatic or heteroaromatic groups. Preferably, A and B are independently selected from optionally-substituted five or more preferably six-membered aromatic and heteroaromatic groups. Preferred heteroatoms of said heteroaromatic groups include nitrogen, oxygen and sulphur atoms of which oxygen and especially nitrogen, are preferred. Preferred heteroaromatic groups include only one heteroatom. Preferably, a or said heteroatom is positioned furthest away from the position of attachment of the heteroaromatic group to the polymer backbone. For example, where the heteroaromatic group comprises a six-membered ring, the heteroatom is preferably provided at the 4-position relative to the position of the bond of the ring with the polymeric backbone.

Preferably, A and B represent different groups. Preferably, one of A or B represents an optionally-substituted aromatic group and the other one represents an optionally-substituted heteroaromatic group. Preferably A represents an optionally-substituted aromatic group and B represents an optionally-substituted heteroaromatic group

especially one including a nitrogen heteroatom such as a pyridinyl group.

Unless otherwise stated, optionally-substituted groups described herein, for example groups A and B, may be substituted by halogen atoms, and optionally substituted alkyl, acyl, acetal, hemiacetal, acetalalkyloxy, hemiacetalalkyloxy, nitro, cyano, alkoxy, hydroxy, amino, alkylamino, sulphinyl, alkylsulphinyl, sulphonyl, alkylsulphonyl, sulphonate, amido, alkylamido, alkylcarbonyl, alkoxycarbonyl, halocarbonyl and haloalkyl groups. Preferably, up to 3, more preferably up to 1 optional substituents may be provided on an optionally substituted group.

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Unless otherwise stated, an alkyl group may have up to 10, preferably up to 6, more preferably up to 4 carbon atoms, with methyl and ethyl groups being especially preferred.

20 Preferably, A and B each represent polar atoms or group -that is, there is preferably some charge separation in groups A and B and/or groups A and B do not include carbon and hydrogen atoms only.

25 Preferably, at least one of A or B includes a functional group which can undergo a condensation reaction, for example on reaction with said second polymeric material. Preferably, A includes a said functional group which can undergo a condensation reaction.

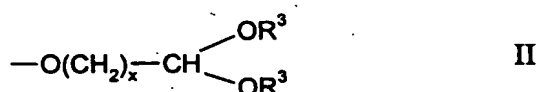
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Preferably, one of groups A and B includes an optional substituent which includes a carbonyl or acetal group with a formyl group being especially preferred. The other one of groups A and B may include an optional substituent which is an alkyl group, with an optionally substituted,

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preferably unsubstituted, C₁₋₄ alkyl group, for example a methyl group, being especially preferred.

Preferably, A represents a group, for example an aromatic group, especially a phenyl group, substituted (preferably at the 4-position relative to polymeric backbone when A represents an optionally-substituted phenyl group) by a formyl group or a group of general formula



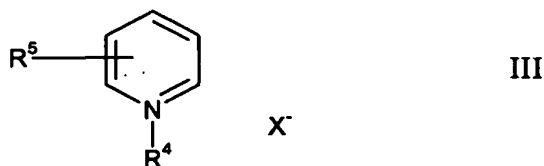
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where x is an integer from 1 to 6 and each R³ is independently an alkyl or phenyl group or together form an alkalene group.

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Preferably, B represents an optionally-substituted heteroaromatic group, especially a nitrogen-containing heteroaromatic group, substituted on the heteroatom with a hydrogen atom or an alkyl or aralkyl group. More preferably, B represents a group of general formula

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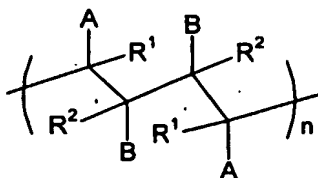
wherein R⁴ represents a hydrogen atom or an alkyl or aralkyl group, R⁵ represents a hydrogen atom or an alkyl group and X⁻ represents a strongly acidic ion.

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Preferably, R^1 and R^2 are independently selected from a hydrogen atom or an optionally-substituted, preferably unsubstituted, alkyl group. Preferably, R^1 and R^2 represent the same atom or group. Preferably, R^1 and R^2 represent a hydrogen atom.

Preferred first polymeric materials may be prepared from any of the compounds described on page 3 line 8 to line 39 of GB2030575B by the method described in WO98/12239 and the contents of the aforementioned documents are incorporated herein by reference.

Said first polymeric material may be of formula



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wherein A, B, R^1 and R^2 are as described above and n is an integer. Integer n is suitably 10 or less, preferably 8 or less, more preferably 6 or less, especially 5 or less. Integer n is suitably at least 1, preferably at least 2, more preferably at least 3. Preferably, formation of said third polymeric material from said first and second polymeric materials involves a condensation reaction. Preferably, formation of said third polymeric material involves an acid catalysed reaction. Preferably, said first and second polymeric materials include functional groups which are arranged to react, for example to undergo a condensation reaction, thereby to form said third polymeric material. Preferably, said first and second polymeric materials include functional groups which are arranged to react for example to undergo an acid

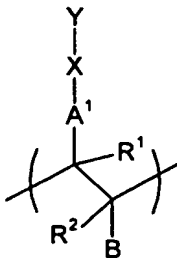
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catalysted reaction thereby to form said third polymeric material.

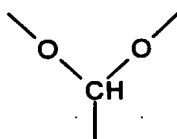
Preferably, said second polymeric material includes a functional group selected from an alcohol, carboxylic acid, carboxylic acid derivative, for example an ester, and an amine group. Said second polymeric material preferably includes a backbone comprising, preferably consisting essentially of carbon atoms. The backbone is preferably saturated. Pendent from the backbone are one or more said functional groups described. Said polymer may have a number average molecular weight (Mn) of at least 10,000, preferably at least 50,000, especially at least 75,000. Mn may be less than 500,000, preferably less than 400,000. Said second polymeric material is preferably a polyvinyl polymer. Preferred second polymeric compounds include optionally substituted, preferably unsubstituted, polyvinylalcohol, polyvinylacetate, polyalkylene glycols, for example polypropylene glycol, and collagen (and any component thereof) and of these polyvinylalcohol and/or polyvinylacetate based polymeric materials are preferred.

Preferably, said second polymeric material includes at least one vinyl alcohol/vinyl acetate copolymer which suitably includes greater than 50%, preferably greater than 65%, more preferably greater than 80wt% of vinyl alcohol moieties.

Said third polymeric material suitably includes a moiety of formula



wherein R^1 , R^2 and B are as described above, A^1 represents a residue of group A described above after the reaction involving said first and second polymeric materials, Y represents a residue of said second polymeric material after said reaction involving said first and second polymeric materials and X represents a linking atom or group extending between the residues of said first and second polymeric materials. In one preferred embodiment A^1 represents an optionally-substituted phenyl group, X represents a group



which is bonded via the oxygen atoms to a residue of said second polymeric material. For example, group X may be bonded to the polymer backbone of said second polymeric material.

According to a second aspect of the present invention there is provided a method of preparing a treatment fluid formulation (e.g. a fracturing fluid) comprising:

selecting a first polymeric material and a second polymeric material as described according to said first aspect; and

causing the formation of a said third polymeric material by a reaction involving said first and second polymeric materials.

The method may include contacting the first and second polymeric materials with an acid for catalysing the reaction thereof.

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The method may include incorporating into the treatment fluid formulation one or more proppants.

The method may include incorporating into the treatment
10 fluid formulation a breaker means. Said breaker means is preferably arranged to cleave 1,2-diol linkages. Said breaker means preferably comprises a periodate.

Preferably, said one or more proppants and/or said breaker
15 means is/are incorporated after formation of said third polymeric material.

In a preferred embodiment, the method comprising contacting said first and second polymeric materials at a
20 weight ratio of first to second in the range 0.025 to 0.067; and contacting the third polymeric material which forms with 5 to 20wt% proppants.

According to a third aspect of the present invention,
25 there is provided a treatment fluid formulation comprising:

- water;
- a third polymeric material as described according to
30 the first and second aspects; and
- one or more proppants.

Said treatment fluid formulation preferably comprises 1 to 5wt% of said third polymeric material, 65 to 90wt% water and 5 to 30 wt% of proppants.

- 5 Said treatment fluid formulation preferably includes a breaking means.

The treatment fluid formulation preferably has a viscosity at 25°C of at least 200 cp, measured at a shear rate of
10 100s^{-1} .

According to a fourth aspect of the invention, there is provided the use of treatment fluid formulation as described herein in hydraulically fracturing a
15 subterranean formation.

According to a fifth aspect of the invention, there is provided a method of breaking a third polymeric material as described herein, the method comprises providing a
20 formulation comprising said third polymeric material and a breaker means (e.g. encapsulated periodate) and causing said breaker means to change its state (e.g. rupture) in order to release an active breaker material arranged to break the third polymeric material.

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According to a sixth aspect of the present invention, there is provided an encapsulated breaker means for a third polymeric material as described herein per se.

- 30 According to a seventh aspect of the invention, there is provided a method of recovering oil from a subterranean formation comprising:

- hydraulically fracturing a subterranean formation as described according to said first aspect;
- allowing an area fractured to close down whilst being propped by a proppant; wherein as a result of said close down, a breaker means releases an active material which is arranged to lower the viscosity of the treatment fluid formulation of the first aspect; and
- allowing oil to flow to the surface after the viscosity of the treatment fluid formulation has been lowered.

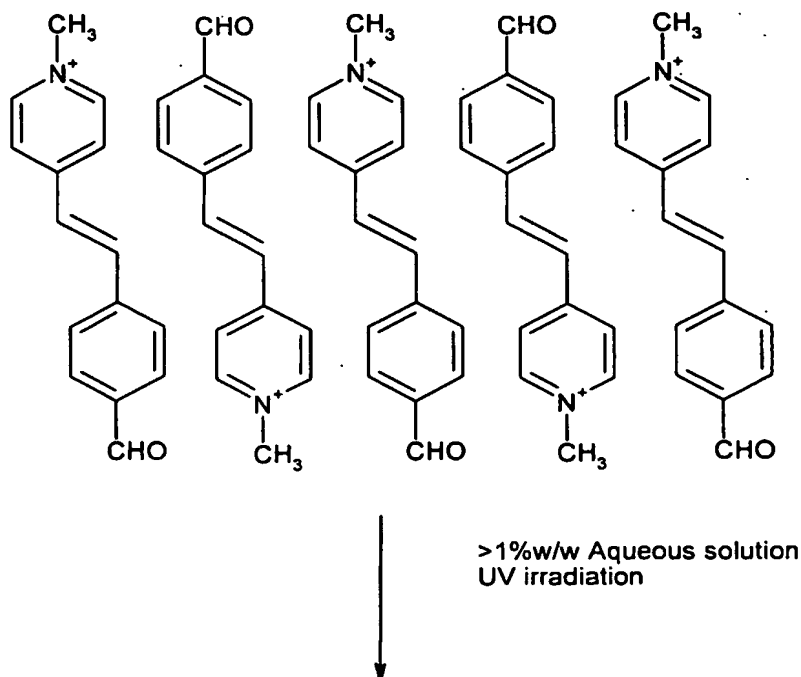
Any feature of any aspect of any invention or embodiment described herein may be combined with any feature of any aspect of any other invention or embodiment described herein mutatis mutandis.

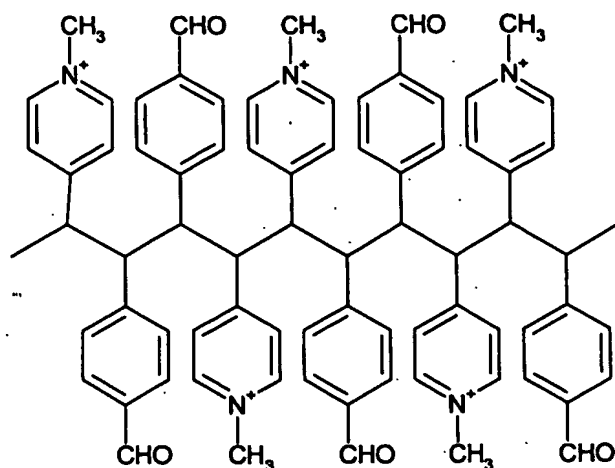
Specific embodiments of the invention will now be described by way of example.

In general terms, fracturing of a subterranean formation may be achieved using a hydrogel. The gel is formed from a gel precursor formulation which comprises an aqueous formulation of poly (1,4-di(4-(N-methylpyridinyl)) -2, 3-di(4-(1-formylphenyl) butylidene), poly (vinyl alcohol) and a suitable proppant, in the presence of an acid catalyst. The gel may be prepared at the surface with a viscosity of greater than 200 cp measured at 100s⁻¹ and then injected into the subterranean formation under high pressure to fracture the formation.

Example 1 - Preparation of poly (1,4-di(4-(N-methylpyridinyl))-2,3-di(4-(1-formylphenyl)butylidene

This was prepared as described in Example 1 of PCT/GB97/02529, the contents of which are incorporated herein by reference. In the method, an aqueous solution of greater than 1 wt% of 4-(4-formylphenylethenyl)-1-methylpyridinium methosulphonate (SbQ) is prepared by mixing the SbQ with water at ambient temperature. Under such conditions, the SbQ molecules form aggregates. The solution was then exposed to ultraviolet light. This results in a photochemical reaction between the carbon-carbon double bonds of adjacent 4-(4-formylphenylethenyl)-1-methylpyridinium methosulphate molecules (I) in the aggregate, producing a polymer, poly (1,4-di(4-(N-methylpyridinyl))-2,3-di(4-(1-formylphenyl)butylidene methosulphonate (II)), as shown in the reaction scheme below. It should be appreciated that the anions of compounds I and II have been omitted in the interests of clarity.





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Example 2 - Preparation of polymer blend

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A blend may be prepared comprising 0.125 wt% of the butylidene polymer of Example 1 and 2 wt% of 88% hydrolysed poly(vinylalcohol) of molecular weight 300,000 in water. Suitably, the poly(vinylalcohol) is added slowly with constant stirring to an aqueous solution of the butylidene polymer so as to disperse the poly(vinylalcohol). Final dissolution may be achieved by maintaining the solution at a temperature of 60°C for a period of 6 hours.

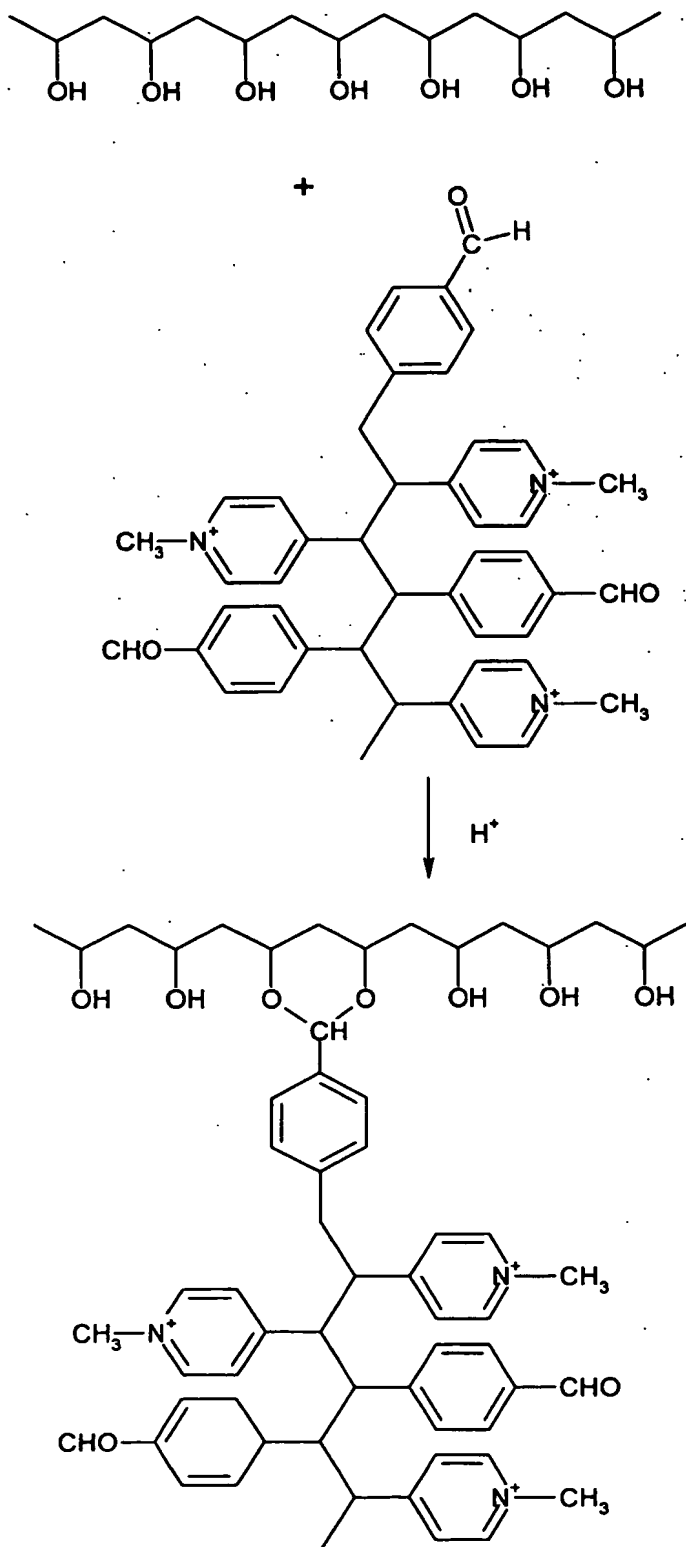
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Example 3 - Preparation of visco-elastic liquid

To the aqueous solution of the polymer blend described in Example 2 was added 0.01 wt% of 0.25M hydrochloric acid. This causes the butylidene and the poly(vinylalcohol) polymers to react according to the scheme below.

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The concentration of acid affects the speed of the reaction and therefore the development of the visco-elastic properties.

- 5 After formation of the visco-elastic liquid 5 to 30 wt% of proppants and 0.05 to 0.3 wt% of an encapsulated periodate breaker is added. Optionally bactericides may be added.
- 10 Using the method and formulation described, a relatively cost effective and clean fluid having low solids content, high thermal stability and good fluid loss properties can be prepared.
- 15 Techniques for injecting the formulation described into a subterranean formation for hydraulically fracturing it are well known to persons skilled in the art. In the method the formulation described is injected into a wellbore under high pressure. Once the natural reservoir pressures
- 20 are exceeded, the fluid initiates a fracture in the formation which generally continues to grow during pumping and the formulation enters the fracture. On removal of the pressure, the fracture tends to close down but is restricted from doing so by the proppant which prevents
- 25 complete closure of the fracture and thereby helps to maintain open a channel which extends from the fracture zone to the wellbore.

Additionally, as the fracture closes down, it will crush

- 30 the breaker (since its particle sizes will be about the same as or greater than those of the proppants) and, consequently, sodium metaperiodate is released which contacts the gel and causes it to break down due to

cleavage of 1,2-diol linkages of the moiety in the gel derived from polyvinylalcohol. Consequently, the viscosity of the gel is substantially reduced whereupon, when the wellbore is opened to the surface oil or gas in the fracture zone can push the broken gel to the surface.

A summary of the properties of a gel formed as described herein includes:

- (a) It is stable in typical sea water obtained from the North Sea.
- (b) It is not affected detrimentally by temperatures of 150°C and above.
- (c) It is stable at temperatures below 0°C and may be prepared and/or applied in cold climates as well as hot.
- (d) It is not affected detrimentally by pressure of 7000 psi and above.
- (e) Good fluid loss properties can be achieved at relatively low solids content.

Attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and which are open to public inspection with this specification, and the contents of all such papers and documents are incorporated herein by reference.

All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination,

except combinations where at least some of such features and/or steps are mutually exclusive.

Each feature disclosed in this specification (including
5 any accompanying claims, abstract and drawings) may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each
10 feature disclosed is one example only of a generic series of equivalent or similar features.

The invention is not restricted to the details of the foregoing embodiment(s). The invention extends to any novel one, or any novel combination, of the features
15 disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.